FORM PTO-1390 (REV 12-29-99)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	U S APPLICATION NO (If known, see 37 CFR 1 5)
Mo-5936/WW-5506	To be Assigned 09/673226

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/02472	13 April 1999 (13.04.99)	20 April 1998 (20.04.98)

TITLE OF INVENTION METHOD FOR ACTIVATING AND DERIVATIZING CELLULOSE

APPLICANT(S) FOR DO/EO/US Thomas Wagner; Klaus-Gunter Pettrich; Erik-Andreas Klohr; Wolfgang Koch; Klaus Szablikowski; Wolfgang Wagenknecht; Fritz Loth; Hendrik Wetzel

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

Preliminary Amendment w/Abstract

529 Rec'd PCT/PTC 13 OCT 2000

U.S. APPLICATION NO (if known, see 37 CFR 1 5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To be Assigned 09/673226	PCT/EP99/02472	Mo-5936/WW-5506

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :	CALCULATIONS PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO $970.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $840.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $690.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) $670.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) $96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	10 - 20 =	0	X $18.00	$ 0.00
Independent claims	2 - 3 =	0	X $78.00	$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $260.00	$ 0.00
TOTAL OF ABOVE CALCULATIONS =				$ 860.00
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also by filed (Note 37 CFR 1.9, 1.27, 1.28).				$ 0.00
SUBTOTAL =				$ 860.00
Processing fee of **$130.00** for furnishing the English translation later than [ ]20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$
TOTAL NATIONAL FEE =				$
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 0.00
TOTAL FEES ENCLOSED =				$ 860.00
			Amount to be refunded:	$
			charged:	$

a. [ ] A check in the amount of $_____ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $860.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

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00157 PATENT TRADEMARK OFFICE

SIGNATURE

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29,426
REGISTRATION NUMBER

PATENT APPLICATION
Mo-5936
WW-5506

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF	)
	) PCT/EP99/02472
THOMAS WAGNER ET AL	)
	)
SERIAL NUMBER: TO BE ASSIGNED	)
	)
FILED: HEREWITH	)
	)
TITLE: METHOD FOR ACTIVATING AND DERIVATIZING CELLULOSE	)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to the examination of the application, kindly amend the enclosed English language translation thereof as follows:

IN THE SPECIFICATION:

Please delete the title of the translated document appearing in page 1 and insert therefor a revised title reading: --Method for Activating and Derivatizing Cellulose--;

And substitute for the present page 17, a page containing an abstract, the enclosed revised page 17 that reads as follows:

--METHOD FOR ACTIVATING AND DERIVATIZING CELLULOSE

ABSTRACT OF THE DISCLOSURE

A process for activating cellulose is disclosed. The process entails the steps (a) dissolving cellulose in water-containing tertiary aminoxide, (b) coagulating the dissolved cellulose and optionally (c) alkalizing the cellulose obtained in (b). The cellulose derivative of the invention exhibits improved solubility and is largely free from fiber and gel particles.--

IN THE CLAIMS:

In Claim 3, line 1, please delete "claims 1 or 2," and insert --Claim 1--, therefor.

In Claim 4, line 1, please delete "any one of claims 1 to 3," and insert --Claim 1--, therefor.

In Claim 5, line 1, please delete "any one of claims 1 to 4," and insert --Claim 1--, therefor.

In Claim 6, line 1, please delete "any one of claims 1 to 5," and insert --Claim 1--, therefor.

In Claim 7, line 1, please delete "any one of claims 1 to 6," and insert --Claim 1--, therefor.

In Claim 8, line 1, please delete "any one of claims 1 to 7," and insert --Claim 1--, therefor.

In Claim 10, line 1, please delete ", capable of being" and in line 2, please delete "according to" and insert therefor --of--.

REMARKS

The present amendment seeks to render the translated application in better conformance with U.S. practice. A page containing the amended Abstract of the Disclosure is enclosed.

An early examination on the merits is respectfully solicited.

Respectfully submitted,

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Process for activation and derivatisation of cellulose

The present invention relates to an activation process for cellulose and a process for derivatisation of the activated cellulose and the cellulose derivatives obtained therefrom. The products produced in accordance with this process are characterised by advantageous properties, such as, for example, improved solubilities.

The accessibility and reactivity of cellulose is known to be influenced by its super-molecular structure. This is characterised by the presence of zones of different degrees of crystallisation, fibrillar crystallites, and the number, size and availability of internal surfaces. Cellulose is insoluble in conventional solvents such as water, dilute acids and alkaline solutions, and also in commercially available organic solvents. Derivatisation in these solvents therefore proceeds, at least at the beginning of the reaction, under heterogeneous conditions. However, initially, the cellulose must be activated in an appropriate manner in order to increase the accessibility and reactivity of the hydroxyl groups in the cellulose.

Known methods for activating cellulose are all directed towards an opening or expansion of the (internal) surfaces, splitting fibrillar aggregates, destroying crystalline regions and altering crystal sizes and crystal modifications. An activating effect on the subsequent reaction of cellulose is achieved, for example, by grinding, irradiation with electrons (DE 2,941,624, microwaves or γ-rays, hydrolysis, oxidation, thermal treatment, freeze-drying or treatment with substances with a swelling action (alkaline hydroxides, amines and amine complexes, ammonia (EP 0,108,991), aqueous solutions of inorganic acids and salts) (Summary in Hans A. Krässig, *Cellulose-Structure, Accessibility and Reactivity,* Polymer Monographs Vol. 11, Gordon and Breach Science Publishers S.A., pages 215-277, 1993).

In the case of the technical production of cellulose ethers, which is at present carried out exclusively under heterogeneous reaction conditions, the cellulose is generally activated by means of a preliminary treatment with concentrated alkaline solutions. The disadvantages of this approach to processing are as follows:

1. even in the case of reactions which require only catalytic quantities of base (e.g. hydroxyl alkylation, sulfo-ethylation or cyano-ethylation), high concentrations of alkaline hydroxides are required to swell and activate the cellulose,

2. as a result of the large quantities of alkali, a breakdown of the cellulose chain and a high salt load is unavoidable when the alkaline solution used is neutralised.

3. complete solubility of high-viscosity cellulose ethers with low degrees of substitution cannot be achieved, and

4. distribution of the substituents introduced along and between the cellulose chains is not even.

As an activating preliminary treatment, in which the native superstructures of the cellulose are destroyed and their crystallinity reduced, the state of the art also suggests the dissolution of the cellulose in appropriate, non-derivatising solvent systems and subsequent precipitation. The solvent systems used in this context were mixtures of sulfur dioxide/dimethylamine/dimethylsulfoxide (A. Isogai, A. Ishizu, J. Nakano, J. Appl. Polymer Sci. 31, pages 341-352, 1986), mixtures of N,N-dimethylacetamide/lithium chloride (JP 59,038,203) and dimethyl sulfoxide/paraformaldehyde (SU 3,453,670).

These cellulose solvent systems have so far not been useful on a technical scale because of their limited dissolving power, particularly in respect of high-molecular-weight celluloses, and the difficult, and in some cases expensive, recovery of the reagents involved.

A further class of cellulose solvents is provided by the tertiary aminoxides. It is known from US-PS 2,179,181 that cellulose is dissolved without derivatisation by certain tertiary aminoxides and that cellulose shaped bodies, e.g. fibres can be obtained by precipitation. As a cellulose solvent for the production of fibres and films, N-methyl morpholine-N-oxide-monohydrate (NMMNO-MH) has recently attracted commercial interest (US-PS 3,447,956; US-PS 4,196,282; EP 453,610; WO 95/11,261).

Starting from the disadvantages of the known processes for derivatisation of cellulose described, the object of the present invention was to develop a process for the activation and optionally the subsequent derivatisation of cellulose, which is characterised by reduced quantities of activation and derivatisation reagents and which allows the commercial presentation of products with improved solubility properties (lower proportion of gel and fibre, very clear solution).

The present invention therefore relates to a process for activation of cellulose comprising the following steps:

a) dissolution of cellulose in a water-containing, tertiary aminoxide with the optional addition of at least one appropriate stabiliser,

b) coagulation of the dissolved cellulose by the addition of an appropriate precipitating agent and

c) optional alkalisation of the amorphous cellulose obtained from step b).

The following are preferably used as cellulose starting materials for the process in accordance with the invention: chemical celluloses, cotton-linters, coniferous wood sulfite, coniferous wood sulfate and/or hardwood celluloses of extremely diverse level of polymerisation.

Aminoxides selected from the group N-methyl morpholine-N-oxide (NMMNO), N-methyl-piperidine-N-oxide, N-methyl-pyrrolidine-N-oxide, N,N-dimethylcyclohexylamine-N-oxide, N,N-dimethyl-ethanolamine-N-oxide and triethylamine-N-oxide, and water (e.g. NMMNO-MH) or mixtures of water and dipolar-aprotic compounds such as in particular dimethyl sulfoxide, N-methyl pyrrolidone, dimethyl acetamide or dimethyl formamide are preferably used as the water-containing tertiary aminoxide.

The cellulose solutions are prepared in a known manner (US-PS 4,145,532; US-PS 4,196,282; EP 452, 610; WO 95/11261) by dissolving the cellulose in a melt of NMMNO-MH at temperatures of 85 to 115°C. The cellulose material is generally stirred into an aqueous solution of NMMNO at room temperature and water is distilled off under vacuum at 85 to 115°C. In dependence upon the level of polymerisation, the concentration of cellulose is from 2 to 20%, preferably 3 to 15%.

In order to minimise a breakdown of the cellulose during the dissolution process, at least one stabiliser is advantageously used. The stabilisers described in EP-A-047,929 are suitable, particularly gallic acid propyl ester. The preferred quantity of stabiliser is 1 wt.%, relative to the quantity of cellulose.

The water-containing aminoxides may contain small quantities of compounds acting as bases such as tertiary amines and/or alkaline hydroxides.

Precipitating agents suitable for the coagulation of the dissolved cellulose are in particular organic solvents such as ether, particularly dimethyl ether, ketones,

particularly acetone, alcohols preferably with 1-6 carbon atoms, particularly methanol, ethanol, 2-propanol or 2-methyl-2-propanol, and acetonitrile or mixtures of these solvents. The organic solvents may contain small quantities of compounds acting as bases such as tertiary amines and/or alkali hydroxides and/or quaternary ammonium bases.

The precipitating agent can be added to the cellulose solution both continuously and also in stages, and is advantageously also used for washing out any residual quantities of aminoxide in the precipitated cellulose.

The activation process according to the invention exhibits the following advantages by comparison with known processes with dissolution activation:

- no influence of residual lignin on the solubility of the cellulose in the pre-activation stage
- simple process design, preparation and processing of the solvent
- lower costs, simple and complete recovery of the activation reagents
- simpler removal of the activation agents from the activated cellulose (no salts)
- no environmental pollution, possibility of an enclosed solvent circuit
- higher dissolving power also for celluloses with high molecular weight
- preliminary swelling (water, water vapour, liquid ammonia), followed by a subsequent replacement of the solvent is not required for preparation of the solvent.

The activation process according to the invention leads to amorphous cellulose with increased reactivity and also allows a direct derivatisation without preceding alkalisation stage (e.g. esterification to form cellulose acetate, -nitrate or -lactate, and/or conversion with isocyanates), whereby improved yields of cellulose derivatives with improved solubility are achieved.

The present invention therefore also relates to a process for derivatisation of cellulose containing the steps:

a) dissolution of cellulose in a water-containing, tertiary aminoxide, with the optional addition of appropriate stabilisers.

b) coagulation of the dissolved cellulose through the addition of a precipitating agent.

c) optional alkalisation of the amorphous cellulose obtained from step b).

d) derivatisation of the amorphous cellulose obtained in step b) or c), optionally in the presence of an appropriate solvent.

Cellulose derivatives are understood to include conversion products of cellulose with appropriate derivatisation reagents such as cellulose ester (e.g. cellulose acetates, cellulose lactates, cellulose nitrates), cellulose ether ester, cellulose carbamate and especially water soluble and/or organo-soluble cellulose ethers such as carboxyalkyl celluloses (e.g. carboxymethyl cellulose), hydroxyalkyl celluloses (e.g. hydroxyethyl- and hydroxypropyl celluloses), carboxyalkylhydroxyalkyl celluloses (such as carboxymethylhydroxyethyl-, carboxymethylhydroxypropyl cellulose), sulfoalkyl cellulose derivatives (e.g. sulfoethyl cellulose, sulfopropyl cellulose, methyl sulfoethyl cellulose, methyl sulfopropyl cellulose, carboxymethyl sulfoethyl cellulose, carboxy methyl sulfopropyl cellulose, hydroxyethyl-

/hydroxypropylsufopropyl-cellulose ether), alkyl celluloses (e.g. methyl cellulose, ethyl cellulose), alkyl hydroxyalkyl celluloses (e.g. methyl hydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxypropyl cellulose, ethylhydroxypropyl cellulose), alkylene celluloses (e.g. allyl cellulose), alkylene alkyl celluloses (e.g. allylmethyl cellulose, allylethyl cellulose), dialkyl aminoalkyl celluloses (e.g. diethyl aminoethyl cellulose), dialkylaminoalkylhydroxyalkyl celluloses (e.g. diethylaminoethylhydroxyethyl cellulose) and binary or tertiary ionic or non-ionic cellulose ethers from the above-named functional groups.

The derivatisation preferably takes place in the presence of the precipitating agent used for coagulation of the dissolved cellulose. Suitable precipitating agents are organic solvents such as 2-propanol, 2-methyl-2-propanol, acetonitrile, acetone, dimethylether, dioxane, methyl chloride, ethyl chloride (etherification, carbamination), and methylene chloride, glacial acetic acid, carboxylic acid anhydrides such as acetic acid, propionic acid and butyric acid anhydrides (esterification) and mixtures of these solvents.

The process for derivatisation of the cellulose according to the invention is preferably implemented as follows:

a) cellulose is dissolved in the aminoxide/water system with the addition of stabilisers,

b) the dissolved cellulose is precipitated out by the addition of organic solvents and attached aminoxide is removed by washing with the solvent used for sedimentation, and

d) the amorphous cellulose obtained in the above manner is converted in the presence of the organic solvent used for the coagulation, whereby step c) (alkalisation) is omitted.

The present invention also provides the cellulose derivatives produced in accordance with the derivatisation process of the invention.

The cellulose derivatives according to the invention exhibit improved solubility and are largely free from fibre and gel particles. Even those cellulose derivatives according to the invention with low degrees of substitution still exhibit an excellent solubility in water and/or organic solvents.

The activation of cellulose according to the invention and the subsequent conversion to cellulose derivatives will be described in greater detail with reference to the following examples.

Exemplary embodiments

Example 1

Activation of cellulose

53 g cellulose (cellulose, DP_{Cuoxam}580, water content 5.7%) were suspended with the addition of 0.75 g gallic acid propyl ester in 2800 g of a 46% aqueous N-methylmorpholine-N-oxide solution (NMMNO). At a temperature of 105°C and 60-65 mbar pressure, 1320 g water were distilled off, thereby dissolving the cellulose. At 85°C, 1500 ml 2-propanol were added to the cellulose solution with stirring. The cellulose sediment was filtered off, washed free of NMMNO with 2-propanol and adjusted in a filter centrifuge to a dry content of approximately 10%.

In the X-ray investigation of the activated cellulose (DP_{Cuoxam}550), the crystalline parts of the starting material could no longer be detected. The water retaining value (WRV) of the activated cellulose was 3.30 cm^3g^{-1}. By comparison, the non-activated starting cellulose had a WRV value of only 0.65 cm^3g^{-1}.

When using cotton linters (DP_{Cuoxam}640, WRV=0.60 cm^3g^{-1}), the water retaining value of the correspondingly activated material was 3.37 cm^3g^{-1} (DP_{Cuoxam}560).

The activated celluloses used were soaked with 2-propanol for the subsequent conversions.

Example 2

Hydroxyethyl cellulose

The activated cellulose (made from linters, DP_{Cuoxam}560) soaked in 2-propanol, was suspended under a nitrogen atmosphere in a 1:1 mixture (w/w) of 2-propanol and 2-methyl-2-propanol (7.5 wt. % cellulose in the suspension mixture), and at 10°C, 0.8 mol sodium hydroxide/mol anhydro-glucose unit (AGU) of the cellulose and 5 mol water/mol AGU were added. After stirring for 160 minutes at this temperature, 2 mol ethylene oxide/mol AGU were added by metered doses and the reaction mixture was tempered for 80 minutes at 25°C. The reaction mixture was then stirred further for 100 minutes at 75°C. After cooling to room temperature, the remaining ethylene oxide was removed under vacuum, ventilated with nitrogen and the reaction mixture was neutralised with acetic acid. The reaction product was filtered off, washed free of salt with methanol and dried in the vacuum. The hydroxyethyl cellulose obtained exhibited a molar substitution level of MS=1.34 (equivalent to a reagent yield of ethylene oxide of 67%) and contained 7% water-insoluble matter.

When non-activated cellulose (Linters, DP_{Cuoxam}640) was used under the same reaction conditions, a hydroxyethyl cellulose with MS=0.33 and a reagent yield of ethylene oxide of 17% was obtained; the aqueous solution contained 81% insoluble fibre and gel particles.

Example 3

Sulfoethyl cellulose

Activated cellulose (made from cellulose, DP_{Cuoxam}1120, dry content 10%) soaked in 2-propanol was suspended with a bath ratio of 1:22 in a mixture of 88.6 vol.% 2-propanol, 4.4 vol.% methanol and 7.0 vol.% water. After addition of 2.4 mol sodium hydroxide/mol AGU, alkalisation was carried out for 80 minutes at 20°C under nitrogen. Then 0.8 mol sodium vinyl sulfonate/mol AGU in the form of 30% aqueous solution were added. Over a period 30 minutes, the reaction mixture was

heated to 70°C and then stirred for 120 minutes at this temperature. After cooling to room temperature, the reaction mixture was neutralised with acetic acid and filtered off. The reaction product was washed free of salt with 70% aqueous methanol and dried at 60°C in an ambient-air drying cabinet. The sulfoethyl cellulose obtained in this manner exhibited a level of substitution of DS=0.19 with a reaction yield of sodium vinyl sulfonate of 24%. The 2% aqueous solution had a viscosity of η=32000 mPas with a shear gradient of D=2.55 s^{-1}.

When non-activated cellulose (DP_{Cuoxam}1620) was used, a sulfoethyl cellulose with DS=0.23 was obtained with a reagent yield of 29%; the 2% aqueous solution contained fibres and gel particles.

Example 4

Carboxymethyl cellulose

90 g activated cellulose (containing 36 mmol cellulose) soaked in 2-propanol with a DP_{Cuoxam}830 were suspended in a 250 ml stirring vessel in a mixture of 98.4 ml 2-propanol, 14.7 ml ,ethanol and 22.8 ml water. At room temperature and under the exclusion of oxygen, 2.6 mol sodium hydroxide/mol AGU of the cellulose were added and stirred for 80 minutes. After the addition of 1.3 mol monochloracetic acid/mol AGU (in 80% aqueous solution), the reaction mixture was heated to 70°C, stirred for 120 minutes at this temperature and cooled to room temperature. The reaction product was filtered off, washed with 80% aqueous ethanol until neutral and free from chloride, and then dried. The degree of substitution of the carboxymethyl cellulose, which formed a clear solution in water, was DS=0.92, corresponding to a reagent yield of monochloracetic acid of 71%.

When non-activated cellulose was used, a carboxymethyl cellulose with DS=0.76 was obtained with a reagent yield of 58.5%; the 2% aqueous solution contained fibres and gel particles.

Example 5

Methyl cellulose

Activated cellulose (made from cellulose DP_{Cuoxam}1270) soaked in 2-propanol, was suspended under a nitrogen atmosphere with a bath ratio of 1:20 in a mixture of 2-propanol, methanol and water in the proportions 18:1:1.5. After the addition of 11 mol sodium hydroxide/mol AGU of the cellulose, the reaction mixture was stirred for 90 minutes at 25°C. Then, 10 mol methyl chloride/mol AGU was added in metered doses, the reaction mixture was heated over a period of 30 minutes to 85°C and stirred for 120 minutes at this temperature. After cooling to room temperature, the pressure was reduced to normal pressure and the volatile fractions were removed in the vacuum. The remaining dry residue was placed into boiling water, neutralised with glacial acetic acid and washed in hot water until salt free. The reaction mixture was filtered while still hot and the residue was dried in the ambient-air drying cabinet. The methyl cellulose obtained had a level of substitution of DS=1.38 with 5% water-insoluble particles.

When non-activated cellulose (DP_{Cuoxam}1620) was used under the same reaction conditions, a methyl cellulose with DS=1.17 and 57% water-insoluble particles was obtained.

Example 6

Cellulose lactate

27.2 g activated cellulose (made from linters, DPC_{uoxam}560) soaked in 2-propanol, dry content 18.35% equivalent to 31 mmol AGU) were suspended at room temperature in 150 ml dimethyl acetamide. The 2-propanol present in the mixture was distilled off quantitatively in the vacuum while stirring. After addition of 4 mol L-lactide (L-3,6-dimethyl-1,4-dioxane-2,5-dione)/mol AGU of the cellulose, the reaction mixture was heated to 130°C and stirred for 5 h at this temperature. Then the reaction mixture was cooled to room temperature, 500 ml water were added and the mixture was filtered off. The residue was washed twice in each case with 500 ml of a mixture of water and acetone (3:1, v/v) and dried at 55°C in the ambient-air drying cabinet. The NMR-spectroscopically determined molar degree of substitution of the cellulose lactate obtained was MS=1.8. The softening point of the product is approximately 230°C (Kofler bench).

When the native starting material (linters) is used, no reaction takes place. In accordance with NMR spectroscopy, the isolated material is an unchanged cellulose I-modification.

Patent Claims

1. Process for activation of cellulose comprising the following steps:

   a) dissolution of cellulose in a water-containing, tertiary aminoxide,

   b) coagulation of the dissolved cellulose by the addition of an appropriate precipitating agent and

   c) optional alkalisation of the amorphous cellulose obtained from step b).

2. Process according to claim 1, wherein aminoxides selected from the group N-methyl morpholine-N-oxide (NMMNO), N-methyl-piperidine-N-oxide, N-methyl-pyrrolidine-N-oxide, N,N-dimethylcyclohexylamine-N-oxide, N,N-dimethyl-ethanolamine-N-oxide and triethylamine-N-oxide, and water or mixtures of water and dipolar-aprotic compounds are used as the water-containing tertiary aminoxide.

3. Process according to claim 1 or 2, wherein the dissolution of the cellulose in step a) is carried out with at least one stabiliser.

4. Process according to any one of claims 1 to 3, wherein

   the dissolution of the cellulose in the water-containing tertiary aminoxide in step a) is carried out in the presence of a dipolar-aprotic compound.

5. Process according to any one of claims 1 to 4,

wherein the dissolution of the cellulose in step a) is carried out in the presence of compounds acting as bases, particularly in the presence of tertiary amines and/or alkaline hydroxides.

6. Process according to any one of claims 1 to 5, wherein

ethers, especially dimethyl ether, ketones, especially acetone, alcohols preferably with 1-6 carbon atoms per molecule, especially methanol, ethanol, 2-propanol or 2-methyl-2-propanol, acetonitrile and mixtures of these compounds are used as the organic precipitating agent in step b).

7. Process according to any one of claims 1 to 6, wherein

the addition of the precipitating agent in step b) is carried out stepwise.

8. Process according to any one of claims 1 to 7, wherein

the solvent in step b) contains compounds acting as bases, particularly tertiary amines and/or alkaline hydroxides and/or quaternary ammonium bases.

9. Process for derivatisation of cellulose, comprising the following steps:

a) dissolution of cellulose in a water-containing, tertiary aminoxide,

b) coagulation of the dissolved cellulose by the addition of an appropriate precipitating agent,

c) optional alkalisation of the amorphous cellulose obtained from step b) and

d) derivatisation of the amorphous cellulose obtained in step b) or c), optionally in the presence of an appropriate solvent.

10. Cellulose derivative, capable of being produced in accordance with the process according to claim 9.

Process for activation and derivatisation of cellulose

Abstract

The present invention relates to an activation process for cellulose and a process for derivatisation of activated cellulose and the cellulose derivatives obtained therefrom, wherein the activation step is carried out in the presence of aminoxides.

METHOD FOR ACTIVATING AND DERIVATIZING CELLULOSE

ABSTRACT OF THE DISCLOSURE

A process for activating cellulose is disclosed. The process entails the steps (a) dissolving cellulose in water-containing tertiary aminoxide, (b) coagulating the dissolved cellulose and optionally (c) alkalizing the cellulose obtained in (b). The cellulose derivative of the invention exhibits improved solubility and is largely free from fiber and gel particles.

COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

METHOD FOR ACTIVATING AND DERIVATIZING CELLULOSE

the specification of which is attached hereto,

or was filed on **April 13, 1999**

as a PCT Application Serial No. **PCT/EP99/02472**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 17 454.3	**Germany**	**April 20, 1998**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occured between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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